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Simulation study of ozone depletion through photolysis mechanism of HCFC-124

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Abstract: Quantum calculation methods like DFT, Ab-initio, and semiempirical have been used to simulate the mechanism of Ozone depletion by HCFC-124 (1-Chloro-1,2,2,2-tetrafluoroethane). Structural properties such as Geometry optimized and single point calculation has been done to understand the configuration interaction singly excited state for all chemical species of the suggested reactions and their transition states. Energetic properties such as total energy, molecular orbital energies, zero point energy, energy gap has been calculated with RHF/6-31G* and Beack88LYP/3-21G(d) methods . Potential energy surface calculation has been determined to evaluate the responsible bond of first initiation cleavage step of photolysis mechanism reaction.

They found C-Cl bond is the most responsible in the photolysis mechanism reactions which is produced chlorine radical and other radicals by energy barrier value of 61.305 kCal mol^{-1} with enthalpy of reaction equal to 78.419 kCal mol^{-1}. The transition state examination of these reactions indicated that chlorine radical is the most probable species than other radicals to depleted ozone by HCFC-124. The depletion reaction is spontaneous and exothermic with enthalpy change of reaction equal to -252.64kCal mol^{-1} and free energy equal to -291.376 kCal mol^{-1} .

Key words: HCFC-124, Ozone, Depletion, Photolysis mechanism, transition state, Calculation methods, Simulation study.

Introduction

The earth's atmosphere is protected from much of the sun's UV-B and UV-C radiation by a layer of ozone (O_3) in the stratosphere, which is strongly absorbed in the 230 to 290 nm region[1]. Ozone is ubiquitous in the atmosphere but its mainly concentrated in the stratosphere between 19 and 23 km above the surface of the earth[2]. Majority of ozone in the stratosphere layer is formed naturally by photolysis of oxygenic molecules under UV-radiation[3]. Human activities during the last century involving particularly a new chemical compounds such as chlorofluorocarbons(CFCs), Halons (H), carbon-tetrachloride (CTC) which leads to the destruction of earth's protective stratospheric ozone layer.[4]

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CFC (chlorofluorocarbon) is a stable compound that is used extensively for air conditioning and refrigeration, Propellants and solvents also for the production of foams. chlorofluorocarbons is the main source of ozone depleting substances in the stratospheric layer, also they contribute to global warming.[5] The production of CFC will phase out in beginning of 1995 under the Copenhagen amendment and the Montreal protocol[6]. A new chemical compounds have been identified to be a replacement to the CFC compound such as HCFC (hydrochlorofluorocarbons) and hydrofluorocarbons (HFC) that's have the same physical-chemical properties to the CFC compound with less stratospheric ozone depletion[7]. HCFC-124 (1-Chloro-1,2,2,2-tetrafluoroethane) is a replacement to CFC-114 one of the most practical CFC compound as refrigeration and fire extinguishing agents . The HCFC-124 has a molecular weight equal to 136.48, and B.P equal to –12.1C°, also ozone depletion Potential relative to CFC-12 equal to 0.04[8].

In the present work quantum calculation methods have been used to estimate the ozone depletion mechanism by HCFC-124, through determining the geometry optimized of the parent compound and for the fragments that's resulted from the photolysis reaction also the transition state . The structural properties are important to understand the chemical reactivity during the potential energy surface calculations. Theoretical calculations give energetic parameters of short-lived reactive intermediate moieties. The calculation of transition state structures is very sensitive to the level of theory and basis sets that's be used [9,10] .

Computational Details

Geometry optimizations were performed at the level of HF/RHF, and density functional theory with an exchange potential Becke 88 and correlation potential LYP that's proposed by lee-yang-parr with 3-21G(d) basis sets. Then, harmonic vibration frequencies were computed to prove that each of the optimized structures is a local minimum on its potential surface[11]. Potential energy surface calculation performed by mapping reactants into products to calculate the activation energy.[12]

Results and Discussion

HCFC-124 (1-Chloro-1,2,2,2-tetrafluoroethane) is a polar compound possess one hydrogen atom, the chemical structure represented in figure 1 . Energetic properties of HCFC-124 have been studied using different quantum calculation methods to estimate the chemical reactivity. Table 1 shows the energetic properties of HCFC-124. The total energy calculation by *Abinitio* method give a value of -583015.8, -585812.9kCal mol^{-1}computed by 3-21G (d), 6-31G* basis set respectively, compared with recent theoretical studies the 6-31G* give nearest value of total energy calculation[13].

The physical properties of HCFC-124 as a display in figure 2,which is approved that the electrostatic potential give a negative charge density appears on the fluorine atom (red color) while the carbon atom appears with positive charge density, also the Homo &Lumo calculation in 2&3 dimension has been computed. The total charge density gives high density centered on the fluorine atom that connected to carbon atom number two.

Table 1
Energetic properties of HCFC-124 computed by different methods*

Type of calculation		Semiempirical		*Abinitio*		DFT/Becke88 LYP
		*PM3 microstate/ 4*4*	*AM1*	*3-21G (d)*	*6-31G**	*3-21G (d)*
Total energy		- 53771.57	-59619.32	-583015.8	-585812.85	-584669.69
Binding energy		-712.9214	-712.5329	-	-	-
Heat of formation		-214.489	-214.101	-	-	-
Molecular orbital energy	HOMO	-9.8055	-7.7162	-244.546	-307.31	-164.909
	LUMO	8.7332	12.2246	121.3469	109.447	57.5026
	E_g	18.5387	19.941	365.892	416.757	222.412
Zero point energy		23.05	23.2777	25.4333	25.0256	22.098
Dipole moment D		1.811	1.739	1.4618	1.565	1.383

*Energy values in kCal mol^{-1} unit.

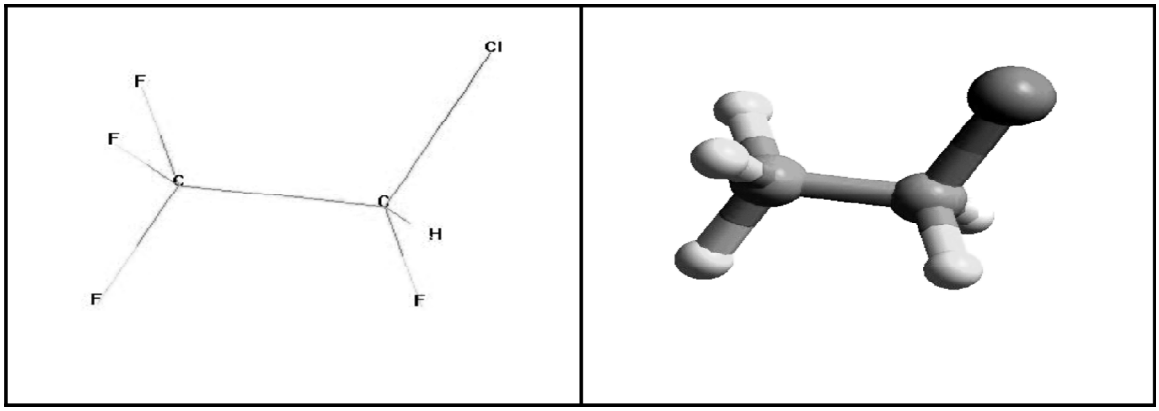


Figure 1: Chemical structure of HCFC-124.

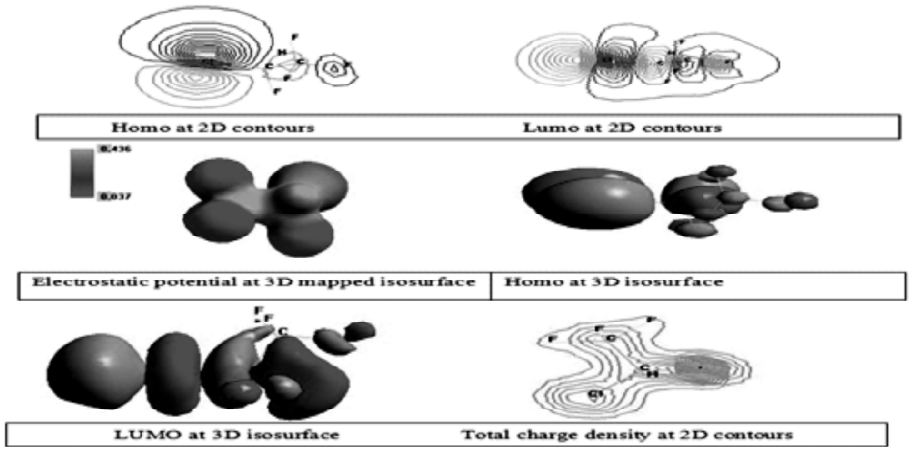


Figure 2: Physical properties of HCFC-124 computed at *Abinitio* /6-31G* method

The bond parameters such as bond length, bond angle of HCFC-124 have been computed using DFT, Ab-initio method which is given a good agreement between the two methods, the C-C bond length computed by the DFT method give nearest value to the experimental value, as shown in table 2,which is equal to 1.542Å and experimental value equal to 1.534Å. The C-F bond length gives a value in the range 1.3-1.35Å which is reaching the experimental value 1.3 Å. The C-Cl bond length equal to 1.74Å calculated by Ab-initio method and the C-H bond length equal to 1.0736 Å which is the same as experimental value[14-16].

Table 2
Structural properties of HCFC-124

Type of calculation		*Ab-initio*	*DFT/Becke 88 lyp*
		3-21G(d)	*3-21G(d)*
Bond lengthÅ	C_1-C_2	1.5	1.542
	C_1-F_1	1.3069	1.344
	C_1-F_2	1.31	1.34
	C_1-F_3	1.3	1.35
	C_2-Cl	1.746	1.814
	C_2-H	1.0736	1.0972
	C_2-F_4	1.332	1.3556
Bond angle degree	C_1-F_1-F_2	108.798	109.621
	C_1-F_1-F_3	109.156	109.082
	C_1-F_2-F_3	108.897	109.203
	C_1-C_2-F_2	108.385	111.472
	C_1-C_2-Cl	110.814	109.12
	C_1-C_2-F_4	107.893	109.757
	C_2-Cl-F_4	109.724	110.212
	C_2-H-Cl	107.936	105.982
	C_2-H-F_4	111.263	112.471

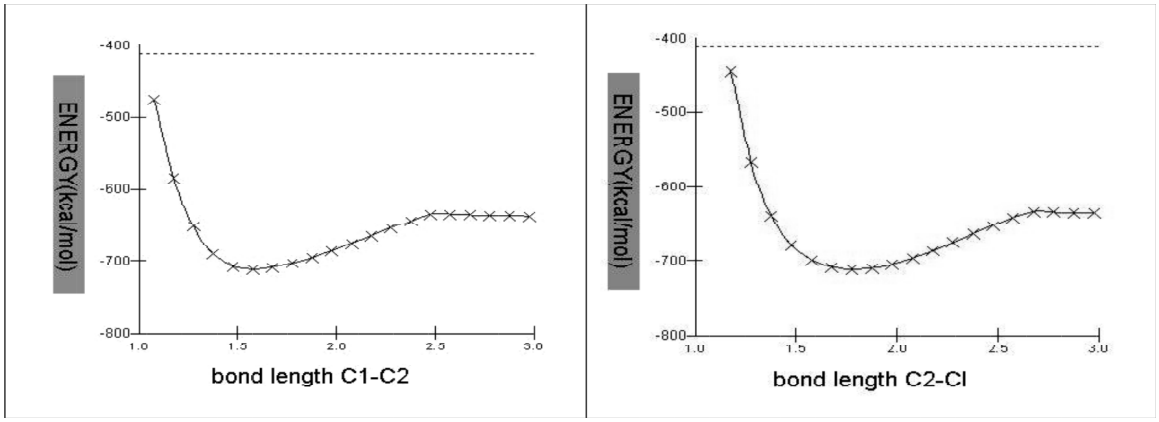
The vibration calculation of HCFC-124 has been computed by both DFT, Ab-initio method which is given 18 normal modes with one positive value of imaginary frequency these normal modes show in table3 which gives good agreement with recent theoretical studies [13].

The potential energy of bond stability has been computed for five types of bonds in HCFC-124 C_1-F_1, C_1-C_2, C_2-H, C_2-F_4, C_2-Cl by using semiempirical- PM3 method as shown in table 4. The C-Cl bond have less value of the dissociation energy with high value of wavelength equal to 407.8643 nm. The C-F bond required less value of wavelength in the range 249.5-250.911 nm, that means high value of energy .

Table 3
Vibration calculation of HCFC-124 computed by different methods

*IR- Frequency**	*Abinitio*	*DFT/Becke 88 LYP*
	3-21G(d)	*3-21G(d)*
υ_1	73.73	58.3
υ_2	199.84	177.14
υ_3	242.79	215.07
υ_4	345.66	301.06
υ_5	414.16	343.79
υ_6	488.65	418.62
υ_7	588.19	505.78
υ_8	642.3	553.24
υ_9	773.47	665.97
υ_{10}	892.25	741.23
υ_{11}	996.09	852.09
υ_{12}	1290.79	1136.36
υ_{13}	1368.94	1180.39
υ_{14}	1459.31	1254.87
υ_{15}	1488.47	1275.82
υ_{16}	1527.85	1307.66
υ_{17}	1602	1391.21
υ_{18}	3400.85	3068.54

The C-H bond, and C-C bond needs wavelength equal to 277.326, 348.5226 nm respectively, with an energy value equal to 96.531, 76.8116 kCal mol^{-1},these values reached the experimental value [17]. The examination of potential energy for bond length stability is represented in figure 3.



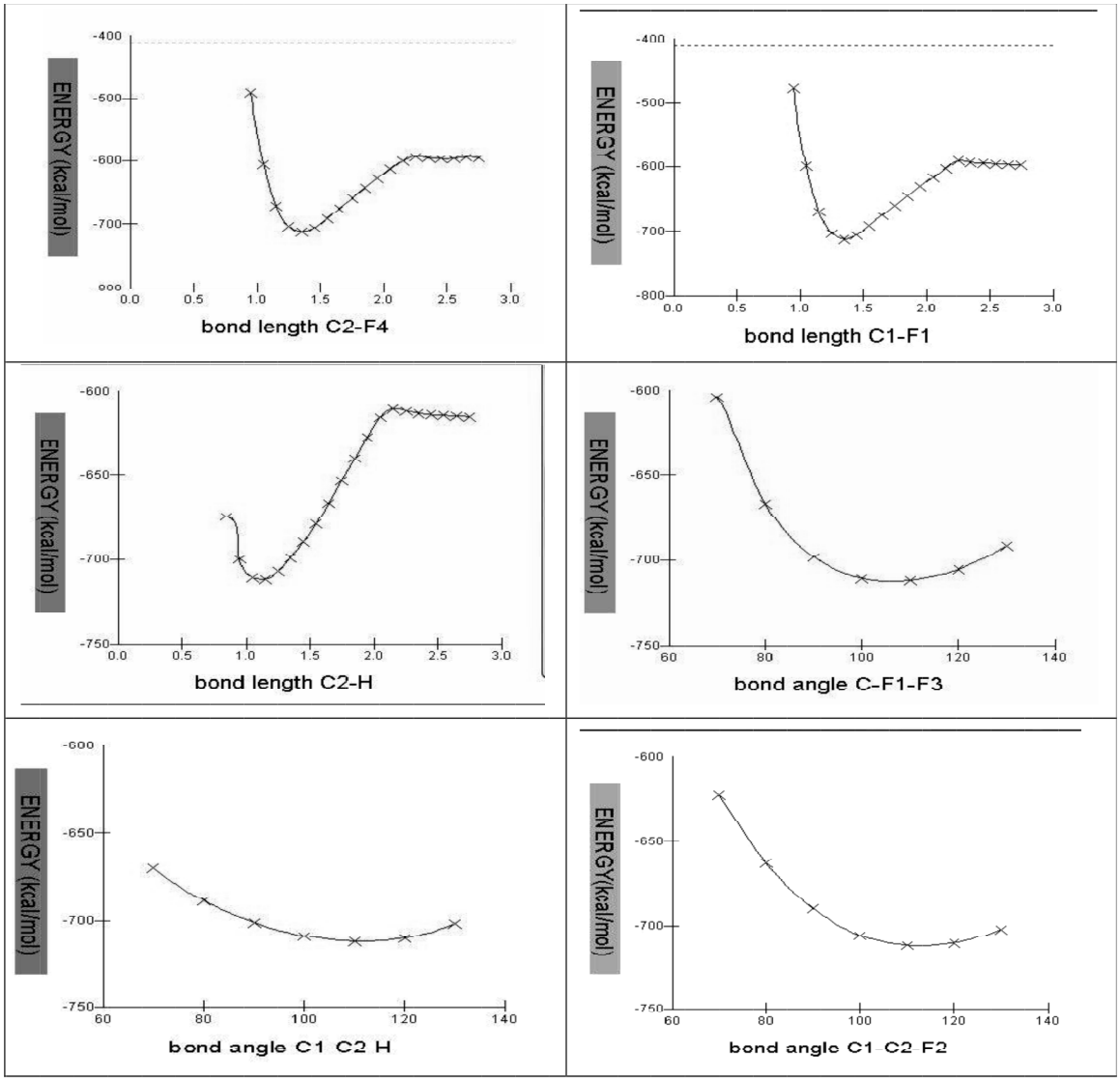


Figure 3: Potential energy search of bonds length & bond angle stability of HCFC-124 computed by semiemprical-PM3 /CI(4*4) microstate.

Table 4
Potential energy of bond stability of HCFC-124 computed by semimperical-PM3 /CI (4*4) microstate

Type of bond	*Equilibrium energy*	*Equilibrium bond length Å*	*Breaking energy*	*Breaking bond length Å*	*Dissociation energy*	*λ nm*
C_1-F_1	-702.933	1.247	-595.6659	2.546	107.267	249.569
C_1-C_2	-711.835	1.576	-635.023	2.47	76.8116	348.523
C_2-H	-711.835	1.147	-614.852	2.55	96.531	277.326
C_2-F_4	-703.283	1.25	-596.589	2.54	106.694	250.911
C_2-Cl	-699.526	1.57	-633.89	2.67	65.636	407.864

* Energy values in kCal mol^{-1} unit

The suggested photolysis mechanism of HCFC-124 occurs through three proposed transition states as represented in figure 4. TS1 through C-Cl bond which leads to the formation of Cl& C_2F_4H , second proposed transition state TS2 is through C-C bond which gives CF_3 &CFHCl, the last proposed transition state is TS3 C-H bond dissociation to give two types of radical H & C_2F_4Cl. The energy barrier & enthalpy of reaction of these proposed transition states given in table 5.

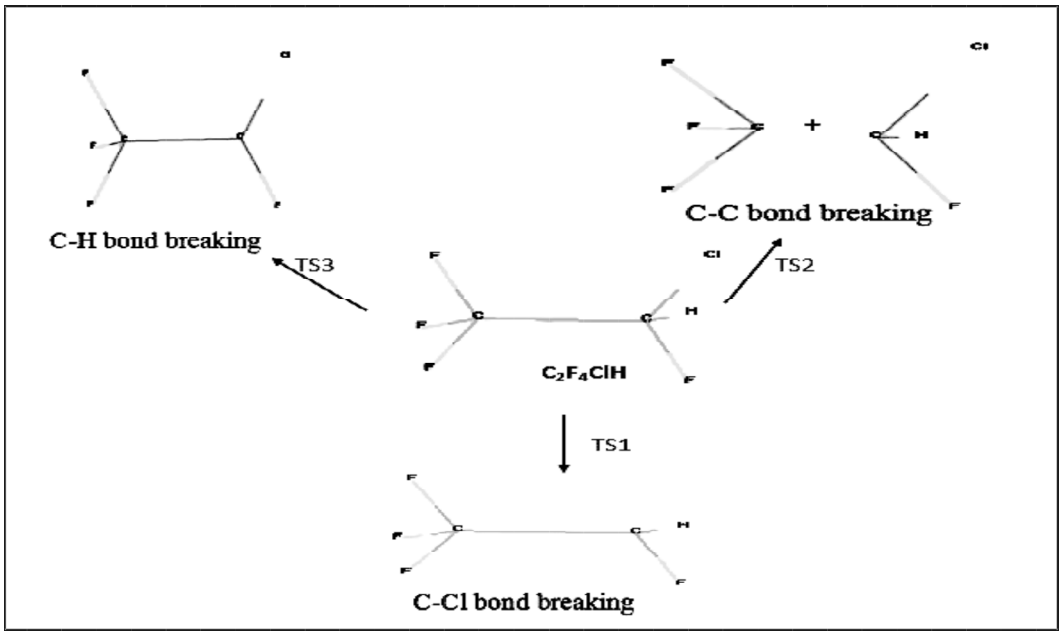


Figure 4: The proposed transition state in photolysis of HCFC-124.

Table 5
Evaluation compares between the proposed transition state of HCFC-124 photolysis, calculated at semiempirical -PM3quatraic states .

Transition States	*Energy barrier**	*Enthalpy change**
TS1	61.3058	78.419
TS2	141.258	63.585
TS3	65.278	78.6245

*Energy values in kCal mol^{-1} unit.

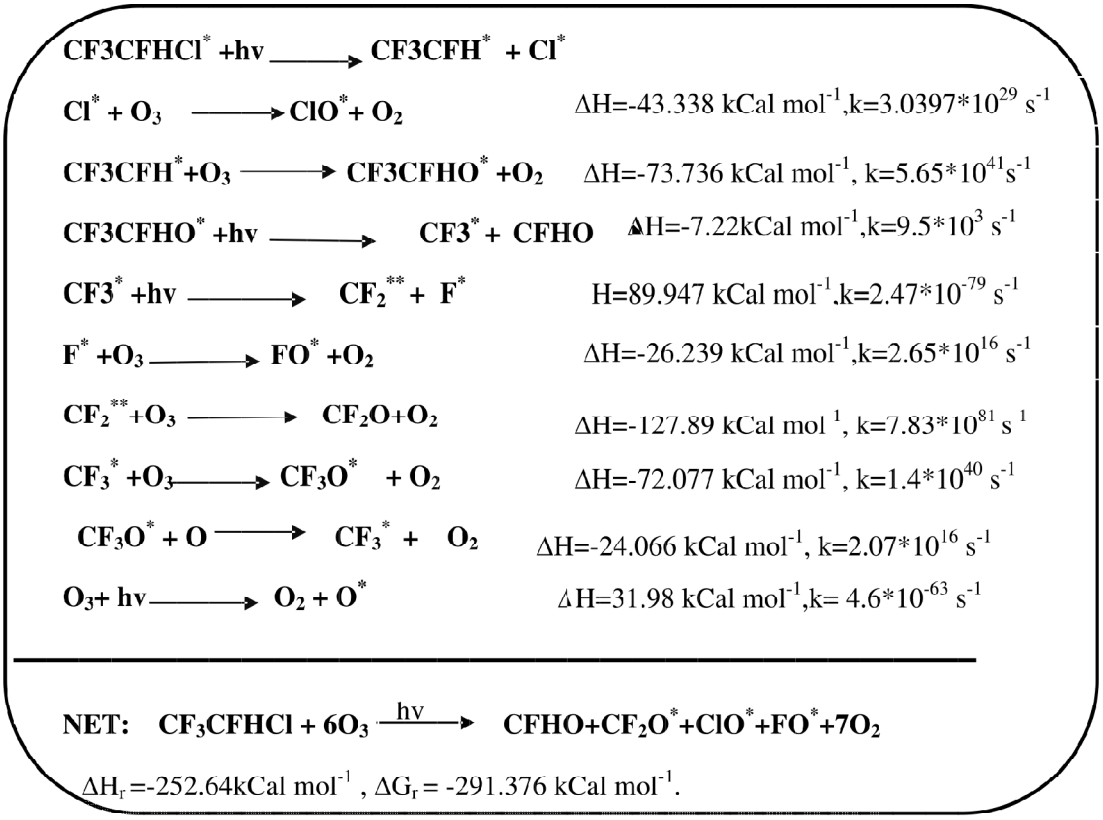
The calculations of potential energy and energy barrier give up an indication, proof that the reaction of C_2F_4HCl molecule occurs through C-Cl bond scission with higher probability than C-C, C-F ,C-H bonds. The photolysis of HCFC-124 under atmospheric conditions will form the $\bullet C_2F_4H$ and Cl• radicals. The suggested reaction, including $\bullet C_2F_4H$ radical formation, that's rapidly react with O_2 to form a peroxy radical ($C_2F_4HO_2$). The radical $C_2F_4HO_2$ will react initially with NO species to produced C_2F_4BrO and NO_2, the energetic values of alkoxy radical shows in table 6 [18].The most probable fate of alkoxy radical is a breakdown of C-C bond to form CF_3 and CFHO[19].

Table 6
Energetic properties of C_2F_4HO radical computed by different methods

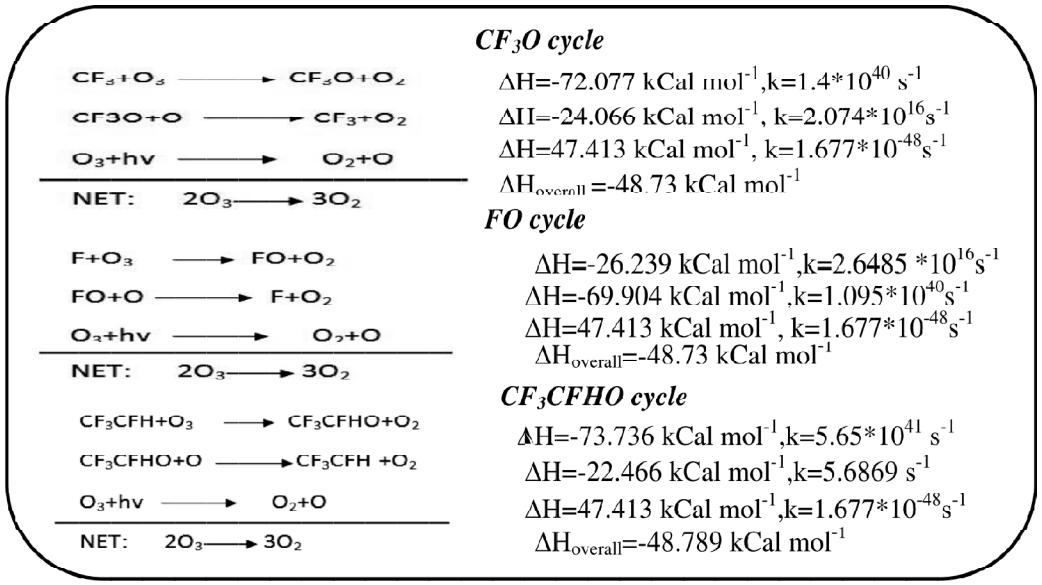
Type of calculation		*Ab-initio /6-31G**	*Semiemprical-PM3*
Total energy		-344438.819	-53204.0208
Binding energy		-	-741.56
Heat of formation		-	-211.9988
Dipole D		1.662	1.901
ZPE		25.5937	23.655
HOMO ev		-14.798	-7.97
LUMO ev		1.711	-0.1117
E_g ev		16.509	7.858
Bond length Å	C_1-C_2	1.525	1.602
	C_2-H	1.0834	1.1187
	C_2-O	1.345	1.3253
	C_1-F_1	1.314	1.344
	C_2-F_4	1.346	1.353
Bond angle degree	C_1-C_2-O	110.505	113.036
	C_1-C_2-H	109.542	111.418
	C_1-C_2-F_4	107.643	108.8
	C_1-C_2-F_1	111.158	112.304
Imaginary frequency		+	+

*Energy values in kCal mol^{-1} unit.

The photolysis mechanism initiated by the reaction of C_2F_4H radical with the ozone molecule to form alkoxy radical with an energy barrier equal to 8.56 kCal mol^{-1} computed at PM3/CI(4*4)microstate and enthalpy of reaction equal to -73.736 kCal mol^{-1} also negative value of free energy change(V) which is equal to -71.941 kCal mol^{-1}. The alkoxy radical undergo secondary photolysis through C-C bond at a wavelength equal to 633.53 nm, this reaction occurs with less value for the enthalpy of reaction which equal to -7.22 kCal mol^{-1}also the rate constant and "G equal to $9.5*10^3$ s^{-1}, -20.413 kCal mol^{-1} respectively. The released fragment in photolysis mechanism will react with ozone in different pathways as represented in scheme1. The rate constant of C-C bond scission reached the experimental value $1.5*10^4$ s^{-1} [20]. The CF_3 radical react with ozone with enthalpy of reaction equal to -72.077 kCal mol^{-1}& "G equal to -69.7514kCal mol^{-1}, the reaction of CF_3 radical with ozone is most likely to produce the CF_3O and any other product would be thermodynamically unstable or would not contribute to ozone depletion[6]. The release radical $*CF_3$, *F, $*CF_3CFH$ will contribute to ozone depletion through $*CF_3O$, *FO, $*CF_3CFHO$ cycle respectively, as shown in scheme 2.



Scheme 1: The proposed photolysis mechanism of HCFC-124 computed by PM3 method



Scheme 2: The *CF_3FO*, *CF_3CFH cycle calculated at Semiempirical- PM3

The geometry optimization of the fragment *CF_2,*CF_2O, *CF_3O, FO*, *CFHO, which resulted in photolysis of HCFC-124 have been computed using PM3 method as represented in table 7.

Table 7
Geometry optimization of fragment resulted from photolysis of HCFC-124 calculated at Semiemprical-PM3 method

Type of calculation		*$*CF_2$*	*$*CF_2O$*	*$*CF_3O$*	**CFHO*	*FO**
Total energy		-23002.02	-29826.61	-39958.09	-19662.1	-16821.1
Binding energy		-257.789	-409.864	-451.76	-33.427	-59.0012
Heat of formation		-49.1193	-141.635	-164.649	-99.039	19.4477
Molecular orbital energy ev	HOMO	-1.0897	-13.295	-9.435	-12.169	-7.9935
	LUMO	2.8837	-0.1264	0.821	0.341	1.869
	E_g	3.9734	13.168	10.256	12.51	9.8625
ZPE		5.291	9.157	11.176	12.758	1.784
IR-frequency cm^{-1}	υ_1	628.46	452.42	285.15	584.76	1236.9
	υ_2	1498.51	459.59	329.57	950.88	-
	υ_3	1569.0	642.29	475.81	1033.8	-
	υ_4	-	1130.22	487.12	1420.58	-
	υ_5	-	1631.11	499.87	1990.43	-
	υ_6	-	2089.55	1036.38	2928.65	-
Bond length Å	C-F	1.2977	1.3216	1.3393	1.3356	-
	C=O	-	1.1986	-	1.202	-
	C-H	-	-	-	1.0971	-
	C_2-F	-	-	-	-	-
	F-O	-	-	-	-	1.3097
	C-O	-	-	1.3578	-	-

*Energy values in kCal mol^{-1} unit

The vibrational calculation of CFHO (formyl fluoride) has been calculated by the same method which is given six fundamental frequencies two with high intensity one for C=O stretching, which is equal to 1990.43 cm^{-1} and the other one for C-F stretching which is equal to 1033.8 cm^{-1} these values reached the experimental value which is equal to 1834 ,1049 cm^{-1} for C=O,C-F stretching respectively [21]. The bond length of CFHO found to be equal to 1.097 Å for C-H bond and 1.34 Å for C-F also 1.202 Å for C=O bond these value reached the experimental value 1.08Å,1.4Å,1.15Å for C-H,C-F,C=O respectively based on electron diffraction data for related molecules[22].

Conclusion

- Depletion of ozone in the stratospheric layer occurs in the presence of HCFC-124 through photolysis of C-Cl bond by energy barrier equal to 61.31 kcal mol^{-1}.

- The reactions of the fragment FO, CF_3O, CF_3CFHO with ozone are exothermic with $\Delta H_{overall}$ fall in the range –(48.73 - 48.789) kCal $mol^{-1.}$
- The photolysis net equation of HCFC-124 show that one mole of HCFC-124 deplete six mole of ozone with enthalpy change of reaction equal to -252.64kCal $mol^{-1}$and free energy change equal to -291.376 kCal mol^{-1}.

$$CF_3CFHCl + 6O_3 \xrightarrow{hv} CFHO+CF_2O^*+ClO^*+FO^*+7O_2$$

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